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Article

Living Radical Polymerization via Organic Superbase Catalysis

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Abstract: Organic superbases reacted with alkyl iodides (R–I) to reversibly generate the corresponding alkyl radicals (R[•]). Via this reaction, organic superbases were utilized as new and highly efficient organic catalysts in living radical polymerization. The superbase catalysts included guanidines, aminophosphines and phosphazenes. Low-polydispersity polymers ($M_w/M_n = 1.1–1.4$) were obtained up to high conversions (e.g., 80%) in reasonably short times (3–12 h) at mild temperatures (60–80 °C) for methyl methacrylate, styrene and several functional methacrylates. The high polymerization rate and good monomer versatility are attractive features of these superbase catalysts.

Keywords: organic superbases; organic catalysts; living radical polymerization; reversible complexation mediated polymerization; radical chemistry; alkyl iodide

1. Introduction

Organic catalysts, in lieu of metal-based catalysts, have gained increasing attention, because many are environmentally benign, easy to handle and attractive alternatives in organic syntheses [1–3]. Metal-free catalytic processes are often practical and serve to broaden synthetic applications. Recent important studies in this field have involved the use of organic superbases, such as guanidines and phosphazenes, as catalysts. They exhibit high reactivity and high selectivity in many reactions, including fine organic transformations [4–7], such as asymmetric Michael addition, esterification and nitroaldol reactions, as well as fine polymer syntheses, such as ring-opening polymerization (ROP) [8]

and group transfer polymerization (GTP) [9]. In all these cases, reactions have been either anionic or condensation reactions, rather than radical-based reactions.

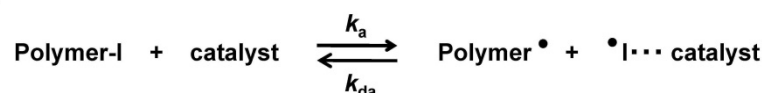
Living radical polymerization (LRP) has become increasingly important in polymer chemistry, because it allows for the synthesis of well-defined polymers with narrow molecular weight distributions [10–20]. LRP is also called reversible deactivation radical polymerization (RDRP). Mechanistically, LRP is based on the reversible activation of a dormant species (Polymer-X) to a propagating radical (Polymer \cdot) (Scheme 1a). A sufficiently large number of activation-deactivation cycles are required for achieving low polydispersity (low dispersity) [21–24]. We recently developed new LRP systems using iodine as a capping agent and organic molecules as catalysts. We developed two mechanistically different systems, referred to as reversible chain transfer-catalyzed polymerization (RTCP) [25–31] and reversible coordination-mediated polymerization (RCMP) [31–35]. These polymerizations are metal-free systems. In this work, we focus on the latter system (RCMP). We previously employed amines, such as triethylamine (TEA) [32,34] and organic salts, such as tetrabutylammonium iodide (BNI) [35], as RCMP catalysts. RCMP involves reversible coordination of the catalyst to Polymer-I to generate Polymer \cdot and the catalyst-iodine complex (Scheme 1b).

Scheme 1. Reversible activation: (a) General scheme and (b) RCMP.

(a) Reversible activation (general scheme)



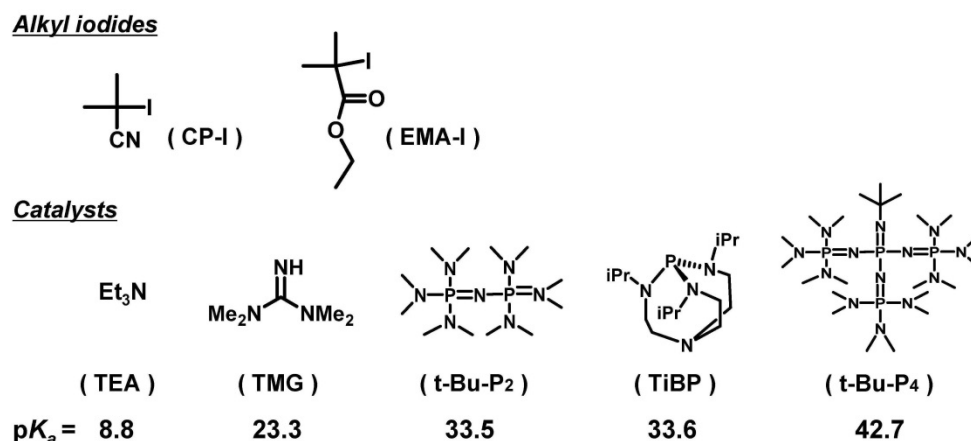
(b) RCMP



We are pursuing more reactive catalysts to widen the scope of RCMP. An important factor of active catalysts is their high ability to coordinate with iodine. As superbases are strong nucleophiles, they may strongly coordinate to iodine and work as active RCMP catalysts. Superbases have not been utilized as catalysts to induce radical reactions, as mentioned. An exploration of the use of superbases in a radical reaction is unique and would be interesting for both organic and polymer chemistry.

In this work, we demonstrate a unique reaction of alkyl iodides (R-I) with superbases to generate carbon-centered radicals (R \cdot) and the application of the superbases as highly active catalysts in RCMP. The superbases studied included a guanidine (TMG), an aminophosphine (TiBP) and phosphazenes (t-Bu-P₄ and t-Bu-P₂) depicted in Figure 1. We studied the polymerizations of methyl methacrylate (MMA), styrene (St) and three functional methacrylates at 60–80 °C.

Figure 1. Structures of alkyl iodides and catalysts used in this work.



2. Experimental Section

2.1. Materials

MMA (99%, Nacalai Tesque, Kyoto, Japan), St (99%, Nacalai), benzyl methacrylate (BzMA) (96%, Aldrich, St. Louis, MO, USA), glycidyl methacrylate (GMA) (97%, Aldrich), and poly(ethylene glycol) methyl ether methacrylate (PEGMA) (average molecular weight = 300) (98%, Aldrich) were purified on an alumina column. 2-Cyanopropyl iodide (CP-I) (99%, Tokyo Chemical Industry (TCI), Tokyo, Japan (contract service)), I₂ (98%, Wako Pure Chemical, Osaka, Japan), TMG (99%, Wako), TiBP (97%, Aldrich), t-Bu-P₂ (2.0 M in THF, Aldrich), t-Bu-P₄ (1.0 M in hexane, Aldrich), TEA (99%, Wako), 2,2''-azobis(2,4-dimethyl valeronitrile) (V65) (95%, Wako), 2,2''-azobis(4-methoxy-2,4-dimethyl valeronitrile) (V70) (95%, Wako), (2,2,6,6-tetramethylpiperidine-1-oxyl) (TEMPO) (99%, Aldrich) and toluene (99.5%, Nacalai) were used as received. Ethyl 2-iodoisobutyrate (EMA-I) (99%) was provided through the courtesy of Godo Shigen Sangyo Co., LTD, Chiba, Japan.

2.2. GPC Measurements

Gel permeation chromatography (GPC) analysis was performed on a Shodex GPC-101 liquid chromatograph (Tokyo, Japan) equipped with two Shodex KF-804L mixed gel columns (300 mm × 8.0 mm; bead size = 7 μm; pore size = 20–200 Å). The eluent was tetrahydrofuran (THF) or dimethyl formamide (DMF) with a flow rate of 0.8 mL·min^{−1} (40 °C). Sample detection and quantification were conducted using a Shodex RI-101 differential refractometer calibrated with solutions of known polymer concentrations. The monomer conversion was determined from the GPC peak area. The column system was calibrated using poly(methyl methacrylate) and polystyrene standards. For the polymerizations of BzMA, GMA and PEGMA, the samples were also detected using a Wyatt Technology DAWN EOS multiangle laser light-scattering (MALLS) detector (Santa Barbara, CA, USA) equipped with a Ga-As laser (λ = 690 nm). The refractive index increment d_n/d_c was determined to be for 0.155 mL·g^{−1} for BzMA (in THF), 0.0962 mL·g^{−1} for GMA (in THF) and 0.054 mL·g^{−1} for PEGMA (in DMF), using a Wyatt Technology OPTILAB DSP differential refractometer (λ = 690 nm).

2.3. NMR Measurement

The NMR spectra were acquired on a Bruker (Karlsruhe, Germany) Avance III (800 MHz) at ambient temperature; ^1H : spectral width 24038.461 Hz, acquisition time 1.9923 s and pulse delay 5.000 s.

2.4. Radical Trap Experiments

A mixture of toluene- d_8 (2.0 mL), CP-I (5 mM), a catalyst (80 mM) and TEMPO (80 mM) was heated in a Schlenk flask at 70 °C for 12 h under an argon atmosphere with magnetic stirring and then quenched to room temperature. The mixtures before and after the heat treatment were analyzed by ^1H NMR.

2.5. Polymerizations

In a typical run, a Schlenk flask containing a mixture of MMA (3 mL), CP-I and a catalyst was heated at 60 °C under an argon atmosphere with magnetic stirring. After a prescribed time t , an aliquot (0.1 mL) of the solution was taken out by a syringe, quenched to room temperature, diluted by THF or DMF to a known concentration and analyzed by GPC.

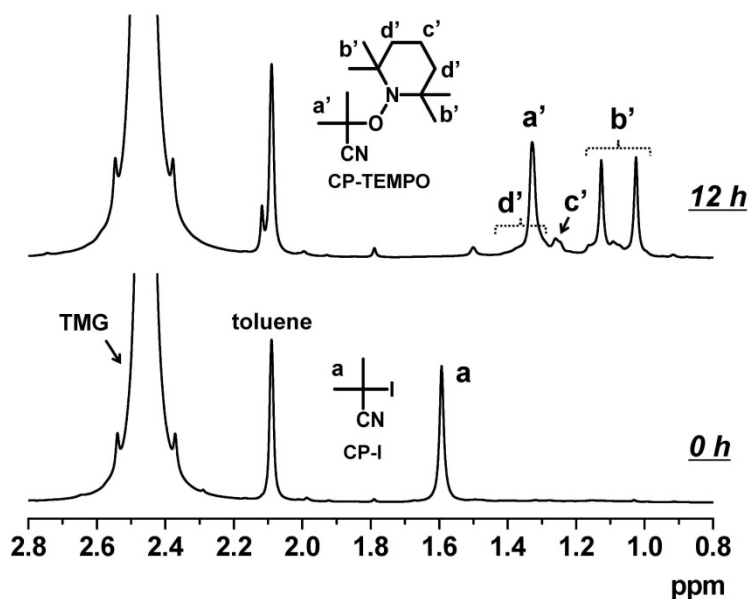
3. Results and Discussion

3.1. Experimental Proof for Generation of R^\bullet from R-I with Superbase Catalysts

A radical trap experiment was performed to demonstrate the generation of a carbon-centered radical R^\bullet from R-I with a superbase catalyst [34–38]. We used CP-I (Figure 1) as R-I and TMG and TiBP as catalysts. In each radical trap trial, we heated CP-I (5 mM), a catalyst (80 mM) and the radical trap TEMPO (80 mM) at 70 °C in toluene- d_8 . If CP-I reacted with a catalyst, the generated radical CP^\bullet would be trapped by TEMPO, thereby yielding CP-TEMPO. Figure 2 shows the ^1H NMR spectra at time zero and at 12 h for TMG. At 12 h, new signals appeared and matched those of pure CP-TEMPO that was independently prepared. The extent of reaction of CP-I to CP-TEMPO was virtually 100% for both TMG and TiBP. The results clearly demonstrate the generation of R^\bullet from R-I with superbase catalysts and at the same time, negligible generation of the corresponding carbon-centered anion R^- .

CP-I can be used as an initiating dormant species in RCMP. The quantitative generation of an alkyl radical from CP-I with TMG and TiBP suggests that TMG and TiBP can be effective catalysts in RCMP. Thus, we attempted to utilize superbases as catalysts for RCMP, as described in subsequent sections.

Figure 2. ^1H NMR spectra (in the range of 0.8–2.8 ppm) of the solution of CP-I (5 mM), TMG (80 mM) and TEMPO (80 mM) in toluene- d_8 heated at 70 °C for 0 and 12 h.



3.2. Polymerization of MMA with TiBP

We carried out the polymerizations of MMA using either TiBP as a superbase catalyst or BNI as a previously studied organic salt catalyst and compared the polymerization results. Figure 3 shows the polymerizations of MMA (8 M) with CP-I (80 mM) as an initiating dormant species and a catalyst (80 mM) at 60 °C. TiBP (open circles) led to 70% monomer conversion after approximately 2 h, whereas BNI (squares) led to the same conversion after approximately 7 h, clearly displaying a much larger polymerization rate R_p in the TiBP system. However, in the TiBP system (open circles), the number-average molecular weight M_n deviated from the theoretical value $M_{n,theo}$ and the polydispersity index (PDI) ($= M_w/M_n$, where M_w is the weight-average molecular weight) was larger than 2.0. This results from an insufficient accumulation of deactivator ($\text{I}_2/\text{catalyst complex}$) in the early stage of polymerization, when many monomers added to Polymer $^{\bullet}$. Thus, we introduced molecular iodine (I_2) as a stating compound, which yields an I_2/TiBP deactivator complex. The addition of I_2 (20 mM) (filled circles) led to good agreement of M_n with $M_{n,theo}$ and a small PDI ($= 1.3$) from an early stage of polymerization. The PDI remained small ($= 1.25$) even at a high conversion (94%), suggesting insignificant side reactions. The R_p with I_2 was slightly lower than that without it (as expected from the equilibrium in Scheme 1b) but was still approximately three times higher than that in the BNI system. These results clearly demonstrate the high reactivity and usefulness of TiBP as a catalyst in RCMP. The results are summarized in Table 1 (entries 1–3).

Figure 3. Plots of (a) $\ln([M]_0/[M])$ vs. t and (b) M_n and M_w/M_n vs. conversion for the MMA/CP-I/catalyst systems (in bulk) (60 °C) (entries 1–3 in Table 1): $[MMA]_0 = 8$ M; $[CP-I]_0 = 80$ mM. The concentrations of catalyst and I_2 and the symbols are as indicated in the figure.

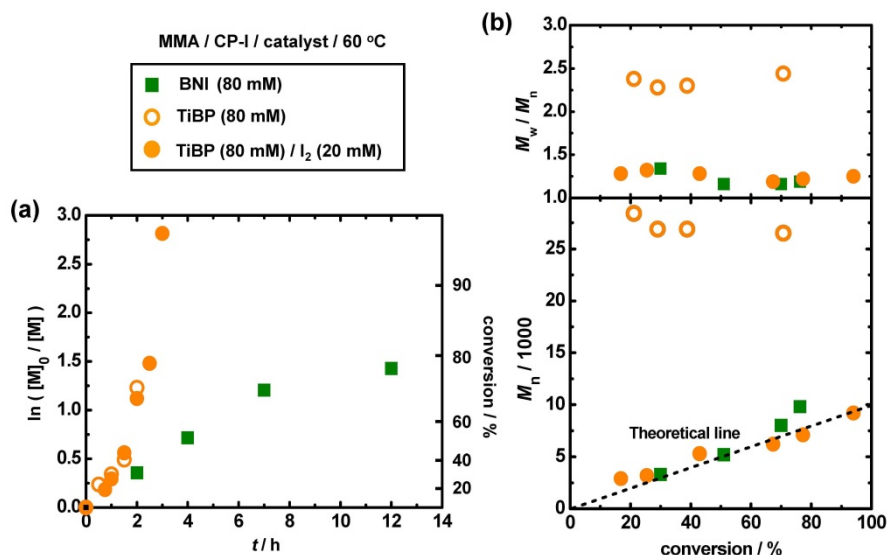


Table 1. Polymerizations of methyl methacrylate (MMA).

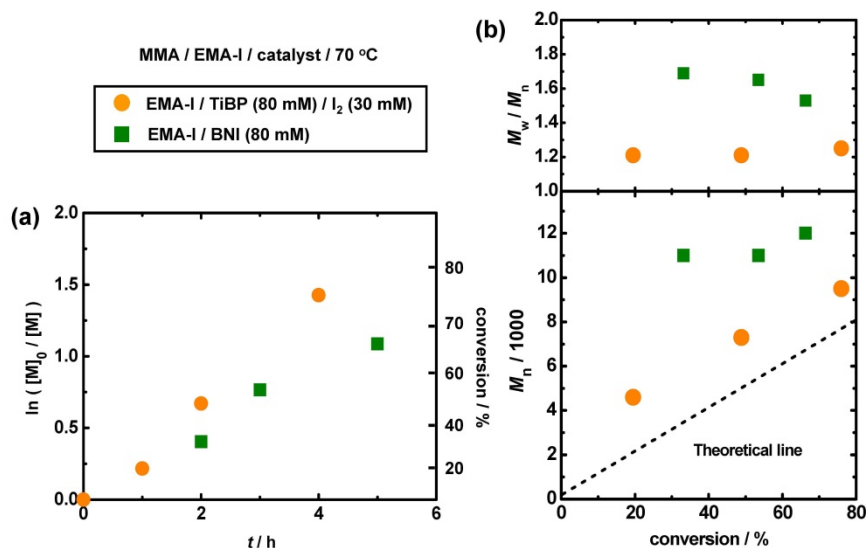
Entry	Target DP	Catalyst	$[CP-I]_0/[catalyst]_0/[I_2]_0$ (mM)	Solvent	t (h)	T (°C)	Conv (%)	M_n ($M_{n,theo}$)	PDI
1	100	BNI	80/80	bulk	7	60	70	8,000 (7,000)	1.16
2	100	TiBP	80/80	bulk	2	60	71	27,000 (7,100)	2.44
3	100	TiBP	80/80/20	bulk	3	60	94	9,200 (9,400)	1.25
4	100	TiBP	80/40/5	bulk	4	60	74	10,000 (7,400)	1.29
5	100	TMG	80/40/5	bulk	12	60	44	6,000 (4,400)	1.13
6	100	TMG	80/80/0	bulk	10	60	63	9,000 (6,300)	1.33
7	100	t-Bu-P ₂	80/40/5	bulk	12	60	76	17,000 (7,600)	1.23
8	100	t-Bu-P ₂	80/40/0	bulk	6	60	64	14,000 (6,400)	1.16
9	100	t-Bu-P ₄	80/40/5	bulk	8	60	82	14,000 (8,200)	1.33
10	100	t-Bu-P ₄	80/40/0	bulk	6	60	65	14,000 (7,000)	1.40
11	100	TEA	80/40/5	bulk	10	60	45	6,300 (4,500)	1.29
12	400	TiBP	20/40/10	Toluene ^a	24	60	91	45,000 (36,000)	1.45
13	400	TiBP	20/80/25	Toluene ^a	14	60	82	38,000 (33,000)	1.20

^a Diluted in 25 wt% toluene (solution polymerization).

3.3. Polymerization from EMA-I

To further probe the high reactivity of TiBP, we studied the polymerizations of MMA with EMA-I (Figure 1) as an initiating dormant species. As the bond strength of EMA-I is higher than that of CP-I, highly reactive catalysts are required for its initiation. Figure 4 shows the polymerizations of MMA with EMA-I using TiBP and BNI catalysts at 70 °C. TiBP afforded good polymerization control, whereas BNI led to a large deviation in M_n and broad polydispersity because of the slow initiation of EMA-I. This result clearly demonstrates that TiBP has a higher activation ability than BNI.

Figure 4. Plots of (a) $\ln([M]_0/[M])$ vs. t and (b) M_n and M_w/M_n vs. conversion for the MMA/R-I/catalyst systems (in bulk) (70 °C): $[MMA]_0 = 8$ M; $[EMA-I]_0 = 80$ mM; $[catalyst]_0 = 80$ mM. The catalysts and the symbols are as indicated in the figure. For the TiBP systems, I_2 (30 mM) was added.



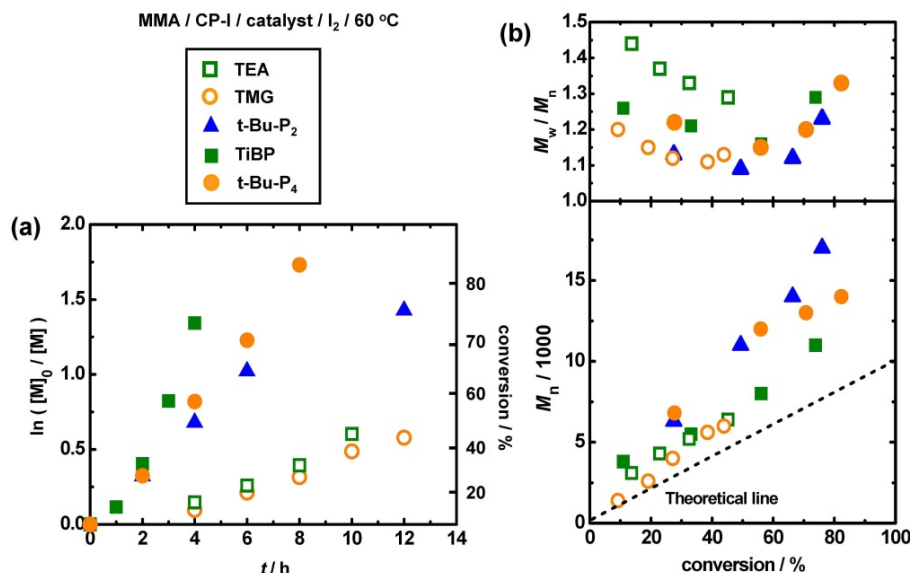
3.4. Other Superbase Catalysts

In addition to TiBP, we examined TMG, t-Bu-P₄ and t-Bu-P₂ as superbase catalysts in RCMP to probe the relationship between basicity and catalytic reactivity in RCMP. We also examined a previously studied weak base catalyst, TEA, for comparison. Among these bases, pK_a increases in the order of TEA ($pK_a = 10.8$) < TMG (23.3) < t-Bu-P₂ (33.5) < TiBP (33.6) < t-Bu-P₄ (42.7) (Figure 1) [39]. Figure 5 and Table 1 (entries 4, 5, 7, 9 and 11) compare the polymerizations of MMA with these catalysts at fixed concentrations of CP-I (80 mM), catalyst (40 mM) and I₂ (5 mM) at 60 °C. Low-polydispersity polymers ($PDI = 1.1$ – 1.4) were obtained up to high conversions in all cases. The R_p was significantly different among the catalysts. As a whole, the higher pK_a systems (t-Bu-P₄, TiBP and t-Bu-P₂) afforded larger R_p than the lower pK_a systems (TMG and TEA). These results clearly demonstrate that higher basicity generally tends to produce higher catalytic activity, as expected. On the other hand, TiBP and t-Bu-P₂ exhibited significantly different R_p despite their similar basicities. This result suggests that the ability of the catalyst to coordinate to iodine depends not only on basicity but also on other factors such as steric hindrance. In an anionic reaction (the coordination to silicon), Kakuchi and Satoh *et al.* also observed a similar general tendency as well as the contribution of other factors [9].

TMG, t-Bu-P₄ and t-Bu-P₂ afforded low polydispersity even without the addition of I₂ (Table 1 (entries 6, 8 and 10)) in contrast to TiBP. In the t-Bu-P₄ and t-Bu-P₂ systems, M_n linearly increased with conversion but was approximately twice as large as $M_{n,theo}$ for reasons that remain unclear.

The obtained results (Figures 2–5 and Table 1 (entries 1–11)) clearly demonstrate the high catalytic reactivities of the superbases. The small PDIs achievable up to high conversions in reasonably short times (3–12 h) are attractive features of these superbase catalysts.

Figure 5. Plots of (a) $\ln([M]_0/[M])$ vs. t and (b) M_n and M_w/M_n vs. conversion for the MMA/CP-I/catalyst systems (in bulk) (60 °C) (entries 4, 5, 7, 9 and 11 in Table 1): $[MMA]_0 = 8$ M; $[CP-I]_0 = 80$ mM; $[catalyst]_0 = 40$ mM; $[I_2]_0 = 5$ mM. The catalysts and the symbols are as indicated in the figure.



3.5. Higher Molecular Weight Polymers and Some Functional Methacrylates

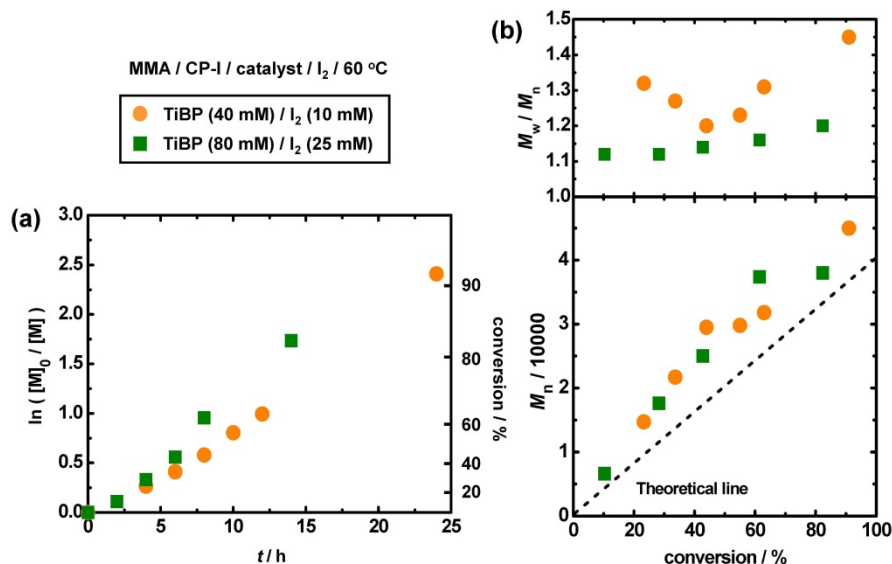
Higher molecular weight polymers were also prepared in the MMA polymerizations. TiBP was used as a catalyst to maintain a sufficiently large R_p . Figure 6 and Table 1 (entries 12 and 13) show examples at a targeted degree of polymerization of 400 at 100% conversion. We obtained low-polydispersity ($PDI = 1.1$ – 1.4) polymers up to a molecular weight of 45,000 in these cases. Table 2 shows the results of the polymerizations of functional methacrylates with benzyl (BzMA), epoxy (GMA) and poly(ethyleneglycol) (PEGMA) groups (entries 3–8) using TiBP and TMG. Low polydispersity polymers were obtained up to high conversion (65%–100%), demonstrating good compatibility with these functional groups.

Table 2. Polymerizations of Functional Methacrylates (in Bulk).

Entry	Monomer	Target DP	Catalyst	$[CP-I]_0/[catalyst]_0/[I_2]_0$ (mM)	T (°C)	t (h)	Conv (%)	M_n ($M_{n,theo}$)	PDI
1	BzMA	100	TiBP	80/40/10	60	8	73	12,000 (13,000)	1.39
2	BzMA	100	TMG	80/80/2	60	30	67	15,000 (12,000)	1.37
3	GMA	100	TiBP	80/10/7	60	9	72	7,500 (10,000)	1.27
4	PEGMA ^a	100	TiBP	80/40/10	60	6	100	19,000 (30,000)	1.36
5	PEGMA ^a	100	TMG	80/40/2	60	6	100	16,000 (30,000)	1.40

^a Molecular weight of monomer = 300.

Figure 6. Plots of (a) $\ln([M]_0/[M])$ vs. t and (b) M_n and M_w/M_n vs. conversion for the MMA/CP-I/TiBP/I₂ systems (60 °C) (entries 12 and 13 in Table 1): $[MMA]_0 = 8$ M; $[CP-I]_0 = 20$ mM. The polymerizations were carried out in 25 wt% toluene. The concentrations of TiBP and I₂ and the symbols are as indicated in the figure.



3.6. Use of Alkyl iodide Formed *in Situ*

In the above-mentioned systems, we employed a preformed alkyl iodide R-I as the starting dormant species. Instead of a preformed R-I, molecular iodine (I₂) and an azo compound (R-N=N-R) can be used as starting compounds and for the polymerization, an R-I formed *in situ* can be used. This method (I₂/azo) was originally invented by Lacroix-Desmazes *et al.* for iodide-mediated LRP [40,41]. We previously showed that this method is effective for RTCP [26,27,30,31] and RCMP [33,35].

Figure 7 (circles) and Table 3 (entry 1) show the polymerization of MMA (8 M) with I₂ (40 mM), V70 (40 mM) and TiBP (20 mM) at 60 °C. V70 affords the alkyl radical R[•] and R[•] reacts with I₂ to yield R-I. Virtually no polymerization occurred after 0.5 h, during which time R[•] had predominantly reacted with I₂ (rather than monomer) and R-I had accumulated. Because the efficiency of V70 to produce free R[•] is approximately 0.6–0.7, 40 mM of V70 can yield about 60 mM of free R[•] and hence about 60 mM (theoretical amount) of R-I. After this period, the polymerization smoothly proceeded (Figure 7). The M_n well agreed with $M_{n,theo}$ and PDI remained small (approximately 1.1) throughout the polymerization.

This method was also successfully applied to higher targeted degrees of polymerization (DPs) (= 270 and 530) in the MMA/TiBP system (Figure 7 (squares and triangles) and Table 3 (entries 2 and 3)). Low polydispersity was achieved up to a molecular weight of 52,000 in this studied case. This method was also effective for another monomer, St and other catalysts (TiBP, TMG and t-Bu-P₄) (Table 3 (entries 4–6)). This method is operationally simple and may be practically useful.

Figure 7. Plots of (a) $\ln([M]_0/[M])$ vs. t and (b) M_n and M_w/M_n vs. conversion for the MMA/I₂/V70/TiBP systems (60 °C) (entries 1–3 in Table 3): $[MMA]_0 = 8$ M. The polymerization was carried out in bulk (for targeted DP = 130 and 270) and in 25 wt% toluene (for targeted DP = 530). The concentrations of I₂, V70 and TiBP and the symbols are as indicated in the figure. V65 (5 mM) was added for targeted DP = 530.

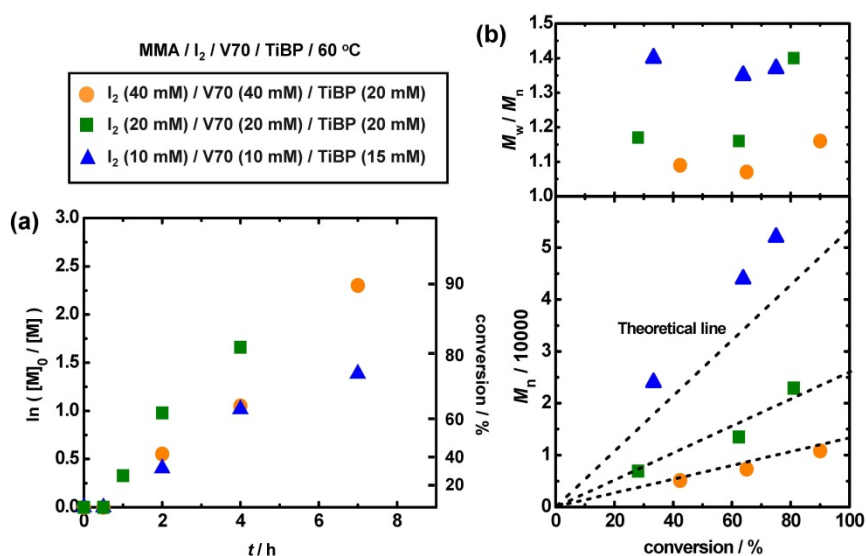


Table 3. Polymerizations of MMA and St with *in Situ* Generated Alkyl Iodine.

Entry	Monomer	Target DP	Catalyst	$\frac{[\text{monomer}]_0/[\text{I}_2]_0}{[\text{V70}]_0/[\text{catalyst}]_0}$ (mM)	Solvent	T (°C)	t (h)	Conv (%)	M_n ($M_{n,\text{theo}}$)	PDI
1	MMA	130	TiBP	8000/40/40/20	Bulk	60	7	95	11,000 (12,000)	1.16
2	MMA	270	TiBP	8000/20/20/20	Bulk	60	4	81	23,000 (22,000)	1.40
3	MMA	530	TiBP	8000/10/10/15 ^a	Toluene ^b	60	23	74	52,000 (40,000)	1.36
4	St	100	TiBP	8000/40/55/20	Bulk	80	7	74	11,000 (7,700)	1.4
5	St	100	TMG	8000/40/50/40	Bulk	80	10	100	12,000 (11,000)	1.4
6	St	100	t-Bu-P ₄	8000/40/60/5	Bulk	80	9	81	11,000 (8,500)	1.38

^a Addition of V65 (5 mM). ^b Diluted in 25 wt % toluene (solution polymerization).

4. Conclusions

R–I reacted with organic superbases to reversibly generate R[•]. With this reaction, the organic superbases were successfully employed as highly reactive catalysts for RCMP. The catalysts enabled the synthesis of low-polydispersity polymers (up to $M_n = 52,000$) through high conversions (e.g., 80%) in reasonably short times (e.g., 3–12 h) at mild temperatures (60–80 °C) for MMA, St and three functional methacrylates. The described catalyst system was free from metals. The facile operation, high polymerization rate and good monomer versatility may be beneficial in a variety of applications.

Acknowledgments

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2-iodoisobutyrate (EMA-I) was provided through the courtesy of Godo Shigen Sangyo Co., LTD, Chiba, Japan. NMR (nuclear magnetic resonance) spectra (Figure 2) were acquired with the NMR spectrometer in the Joint Usage/Research Center (JURC) at Institute for Chemical Research, Kyoto University.

Conflicts of Interest

The authors declare no conflict of interest.

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